AD/A-000 229

ELECTRONIC AND RADIATION DAMAGE PROPERTIES OF RUTILE

Utah University

Prepared for:

Advanced Research Projects Agency

1974

UNIVERSITY OF UTAH
DEPARTMENT OF PHYSICS
SALT LAKE CITY, UTAH 84112

FINAL REPORT

FOR PERIOD 30 JUNE 1970

through

31 JULY 1974

Principal Investigators

John W. DeFord   (Phone 801 581-8396)
Associate Professor of Physics

Owen W. Johnson   (Phone 801 581-7166)
Associate Professor of Physics
and
Adjunct Associate Professor of Materials Science and Engineering

Franz Rosenberger   (Phone 801 581-8373)
Assistant Professor of Physics
and
Director of Crystal Growth Laboratory

Title

ELECTRONIC AND RADIATION DAMAGE PROPERTIES OF RUTILE

i

TABLE OF CONTENTS

I. INTRODUCTION

We have attempted in this final report to provide an overview of the entire project, and to put the work we have done in perspective. To achieve this end, we have avoided technical details, which are contained in the attached preprints and in papers and reports previously submitted, and have tried to make the discussion as general as possible, concentrating primarily on the significance of our results. The present section of the report is mainly a survey of the state of knowledge about TiO_2 and related systems, designed mainly to identify the important problems and to relate them to the long range goals of the project.

As stated in our original proposal, a major long range goal has been to understand the electronic properties of rutile and thus to permit investigation of its feasibility as a device material. In addition, from a more fundamental standpoint, rutile is an excellent model system for the study of wide gap semiconductors in general. It is an exceedingly complex crystal, but it is this complexity which is at the heart of its value as a model system. Much of the complexity arises from the fact that a wide variety of impurities will diffuse in rutile at moderate temperatures. This makes possible the study of many impurity effects which are important in all such materials, but are not readily studied in most related systems, in which the impurities have to be grown in. However, the complexity of TiO_2, coupled with the great difficulties of sample handling, preparation and characterization, demands a different approach than that generally used in solid state physics research. Basically, one must become an expert on the material rather than on the measurement techniques. Sophisticated techniques are

needed, but the main specialization required is a broad and very detailed knowledge of the material. The complex interrelationships of various properties of these systems, such as the strong dependence of impurity solubility and diffusion on the electronic state of the system (which will be discussed below), require a very broad approach to achieve significant progress. Understanding is likely to advance only on a fairly uniform front, rather than in one area of study at a time. Hence, it is important to sort out the problems that are "ready for solution" at a given time. One cannot simply trundle up the technique he wishes to use and fire it at the crystal and expect meaningful results. Knowledge about the system must first have reached the level where the particular problem can be solved, and a great deal of experience is essential to avoid the many pitfalls.

Even a cursory survey of the literature would quickly yield numerous examples illustrating this point. Failure to properly characterize sample material has been a particularly common failing; there are a great many measurements which could be carried out (and often have been), but which would be essentially meaningless due to lack of knowledge as to impurity content, Fermi level, etc. Thus, one of the obvious needs is for development of sample characterization techniques. There are also, of course, many experiments which would be pointless if carried out on presently available crystals, even if they were thoroughly characterized; generally, measurements aimed at determination of properties of the perfect lattice req   .e elimination of impurities, rather than simply a list of which ones are present. Thus, it is also clear that higher quality sample material is needed. This, of course, was the reason for including crystal growth as part of our program. A preliminary survey of the behavior of field-effect transistors which we

fabricated at the beginning of this project is a good example of the need to do things in the proper order; these effects met with very limited success. Functional devices were made, but their behavior was very erratic and unpredictable.[1] These results, coupled with a variety of dielectric loss and other electronic measurements, quickly convinced us that there were very fundamental aspects of the behavior of this system which were simply not understood, and that significant progress toward evaluation of electronic behavior could only be made through a detailed study of the behavior of impurities and defects.

In a wide-gap material such as rutile the information necessary to understand the electronic properties can be divided into two main categories. One, of course, is the properties of the conduction band or bands, which is one of the perfect lattice properties referred to above. The other is detailed knowledge as to the source of the carriers in these bands; with a band gap of 3 eV, it is obvious that the electronic properties will be determined mainly by the impurities and lattice defects present (in a perfect crystal, the room temperature resistivity would be $>10^{24}$ ohm-cm and for all practical purposes the material would be a perfect insulator). We will consider the question of the conduction band properties first.

In a "normal" material such as a metal or most semiconductors what is needed in this category is the "shape" of the conduction band (by this we mean, of course, energy vs. wave number in the Brillouin zone) and hence, the effective density of states in the conduction band, the conduction electron drift mobility, and the corresponding properties of any other accessible bands (such as the valence band).

-3-

In the case of rutile, a fundamental difficulty immediately arises; the electron-phonon interaction is so strong that ordinary band theory is no longer adequate and polaron theory must be used. Apparently, the interaction is sufficiently strong that small polaron theory is required, but not so strong that it fits the approximations of the present theory.[2] The question of whether electronic conduction is by a small polaron mechanism is a subject of great controversy, primarily because the drift mobility has not been measured directly.[2] The Hall mobility is fairly well known,[3] but in small polaron theory Hall and drift mobilities are not equal and their relation to each other is not clear.[4] The clearest theoretical predictions concern the drift mobility in the hopping regime and this has not been measured. Hence, the exact nature of the charge carrier in rutile is poorly understood.

Whether or not the present small polaron theory is applicable, it is still necessary to know the density of states in the conduction "band". A band "shape" in the usual sense may not be a meaningful concept, but an "effective density of states" in the Fermi-Dirac or Boltzmann statistics sense is still a vital parameter in describing the system. Only an order of magnitude value is available for this parameter.[5]

The same considerations would of course apply to valence or impurity band conduction. However, it has not been clearly established whether significant conduction ever occurs in bands other than the conduction band.

It is clear from the above discussion that the key to understanding the conduction mechanism in this system is some means of measuring the electron (or hole) concentration in a given band and of determining the position of the electron Fermi level. This would make possible a direct

measurement of drift mobility, since conductivity measurements are not particularly difficult, and thus a direct comparison with small polaron theory would be possible. Measurement of conduction electron concentration as a function of temperature yields the effective density of states.[6] Conductivity measurements in crystals with a lower Fermi level so that trapping levels are partially empty, makes possible an investigation of impurity band conduction. With a still lower Fermi level, valence band conduction could be studied, if it exists. Thus, the capability of measuring and controlling the electron Fermi level assumes major importance in these systems.

The additional information needed, as previously mentioned, is the source of the carriers and the trapping levels present in the forbidden gap. The carriers and traps arise from two possible sources, lattice defects and impurities. We will consider defects first. The most obvious question to be answered concerning defects is their identity. It appears that only an oxygen-deficient deviation from stoichiometry is possible in rutile.[7] "Reduction" could involve either of two "simple" defects -- Ti interstitials or O vacancies. In addition, of course, various complexes of these defects and/or impurities are conceivable and there exists the possibility of multiple charge states for the defects. There has long been great controversy as to whether O vacancies or Ti interstitials are the dominant defect produced by "vacuum reduction."[8] During the course of the project we have shown that "vacuum" reduction does not occur at a measurable rate below 1000°C.[9] What does occur is impurity (e.g., pump oil) reduction due to dirty vacuum systems. This impurity contamination coupled with poor sample characterization, in general, has plagued attempts to determine unambiguously the identity of the defect. In addition, as will be discussed below, failure to

take account of the importance of Fermi level shifts invalidates even work done on well characterized crystals. The result is that the identity of the defect is not known with certainty.

Once the identity of the defect or defects is known, the trapping levels associated with it must be determined along with the thermodynamic parameters needed to characterize it. Thus, as will be discussed in Section IIB, the thermodynamics of the system must be correctly worked out, including Fermi level effects, in order to achieve any real understanding of defects in such a system.

Many of the same considerations, of course, apply also to impurities. It is immediately clear that a detailed knowledge of solubilities, trapping levels, and charge states of at least major impurities is essential. One of rutile's interesting and rather unusual properties is that a given impurity can exist in several different charge states. For example, we have identified 4 different charge states of Mo in TiO_2.[10] This greatly complicates the thermodynamics of the system and again requires a very careful analysis of the effects of changing Fermi level. These effects have been largely overlooked and yet are of overriding importance in a wide variety of physical phenomena. For example, diffusion is frequently governed by these Fermi level effects rather than by concentration gradients.[11] In fact, such commonly measured quantities as solubilities, diffusion coefficients, charge states, etc., do not even have unique values in such materials.[6] The solubility of H, for example, can be varied by many orders of magnitude at constant temperature by changes in the electron Fermi level.[12] This dependence of diverse physical properties on Fermi level is the essence of the thermodynamic and diffusion work discussed in Sections IIA, IIB, and IIC.

II. RESULTS OF TiO_2 RESEARCH PROGRAM

Prediction of the behavior and effects of both impurities and defects is, of course, fundamentally a question of thermodynamics. Several studies of the defect thermodynamics of TiO_2 had previously been done by other groups.[13] Unfortunately, the results were not conclusive or even consistent. In analyzing this work, we found, in addition to a variety of experimental shortcomings, a very fundamental flaw in the analysis of the data. In a wide gap semiconductor or insulator, the electron Fermi level can readily shift by a substantial fraction of the gap energy, as a result of changing concentrations of impurities or defects. Since the solubility of a given impurity or defect directly involves the Fermi energy (this point is discussed in detail below), it is obvious that any meaningful analysis of the thermodynamics of such a system must take proper account of variation of the Fermi level. Nevertheless, we found that all of the data has been analyzed with the implicit assumption of a constant Fermi energy. To our considerable surprise, we found the same state of affairs existed for all of the systems of this type which had been studied. Thus, our first major undertaking was the reformulation of the defect and impurity thermodynamics of these systems, and programs were initiated to develop the experimental techniques required to verify our theoretical predictions and to measure the thermodynamic parameters required to apply the theory to TiO_2. This phase of the program is discussed in Section A and B below.

A closely related problem (which has also been largely overlooked) is the effect of variation of the electron Fermi level on mass transport phenomena. In situations in which there are enough mobile electrons to quickly equalize the Fermi level throughout the system, there arises the

possibility of internal electric fields due to spatial variation of impurity or defect concentrations, or due to contact with electrode materials having work functions different from that of TiO_2. The presence of such electric fields would, of course, strongly influence the motion of any charge defects or impurities in the system. Conversely, motion of charged ions would result in variation of E_F and hence, would alter the internal fields. Thus, we were confronted with a complex theoretical problem requiring a self-consistent treatment, as well as a detailed knowledge of impurity concentrations, trapping levels, etc. The analysis of this problem proved to be an extremely formidable undertaking. Successful completion of the theoretical formulation, development of adequate computer programs for data analysis, and detailed experimental verification of theoretical predictions for the case of H diffusion in TiO_2 was a major triumph. This aspect of our work and closely related dielectric loss measurements are described in Section C.

The progress we have made in both of these areas in achieving a quantitative understanding of the TiO_2 system should contribute significantly to meaningful evaluation of its potential usefulness for the various applications that have been suggested. However, the significance of the work is by no means limited to TiO_2, since many of our results apply with only minor modifications to virtually any material with a band gap greater than ~1 eV. We expect our results to have a major impact on this part of the materials science field.

A. **Impurity Thermodynamics.**

The simplest and also the most important impurity in TiO_2 is H. H enters the lattice as a singly charged cation interstitial. There apparently

-8-

is a very shallow electron trap associated with the H^+, but it is not occupied to any significant extent above $10°K$ [14] and it is unimportant for present purposes. To maintain charge neutrality, the H^+ must be accompanied by an electron, which, from a statistical point of view, enters the lattice at the Fermi level. Individual electrons may enter either in the conduction band or in any of the various impurity trapping levels, which may be 2 eV or more below the conduction band. It is the effect of this variability of the possible electron energies which has previously not been properly treated.

For purposes of illustration, let us assume that a crystal is to be equilibrated in an atmosphere consisting of known partial pressures of water and oxygen, P_{H_2O} and P_{O_2}, repectively. The reversible reaction describing the H doping is:

$$H_2O(g) \leftrightarrow 2H^+ + 2e^- + \tfrac{1}{2}O_2(g) \tag{1}$$
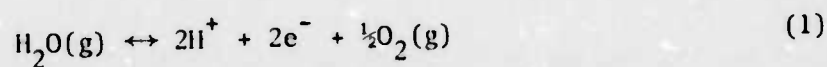
where H^+ represents an interstitial proton and e^- is an electron, in whatever energy state is accessible. In the usual treatment of this problem, Eq. (1) leads to an expression for the equilibrium concentration of H, N_H, given by

$$N_H = F \frac{P_{H_2O}^{1/2}}{P_{O_2}^{1/4} n_e} \tag{2}$$

where n_e is the concentration of electrons (note that this is not even a very well-defined concept, since it is not clear how many of the 10^{23} electrons already present in the crystal should be counted). F is a known function involving temperature, T, the binding energy of an H^+ in the lattice, E_B, and various known thermodynamic parameters of H_2O, O_2, etc.

Eq. (2) is usually further simplified by assuming that $n_e = N_H$, leading to

$$N_H \propto \frac{P_{H_2O}^{\frac{1}{4}}}{P_{O_2}^{\frac{1}{8}}} \tag{3}$$

Alternatively, it is sometimes assumed that n_e is essentially constant, leading to[6]

$$N_H \propto \frac{P_{H_2O}^{\frac{1}{2}}}{P_{O_2}^{\frac{1}{4}}} \tag{4}$$

Neither of these assumptions is defensible and it is very difficult to concoct even very artificial situations in which either Eq. (3) or (4) would accurately predict the behavior of such a system.

Proper treatment of the electron statistics leads instead to an expression for N_H in terms of the electron Fermi level, E_F, which is measured relative to some external reference level:[6]

$$N_H = G \frac{P_{H_2O}^{\frac{1}{2}}}{P_{O_2}^{\frac{1}{4}}} e^{-E_F/kT} \tag{5}$$

Here again, G is a known function which depends on the same parameters as F in Eq. (2) and also on the conduction band density of states. Clearly, the predictions of Eq. (5) are quite different from those of the preceeding ones; since E_F may vary over a range of 2 eV or more, and kT is ~.06 eV at typical diffusion temperatures, the exponent in Eq. (5) could be varied by as much as 32 by changing the electron trap density (for example, such a comparison would fairly accurately describe the difference between a pure crystal and one heavily doped with Al). Thus, the concentration of H for a given ambient

and temperature could vary by as much as a factor of $e^{32} \approx 10^{14}$!
Thus, our previous statement that the effect of E_F on the thermodynamics
of such a system is of overriding importance is, in fact, a very con-
servative appraisal of the situation.

The analysis for other impurities is quite similar to that discussed
above, although the situation can be somewhat more complicated as a
result of trapping levels associated with the impurities or by the possibility
of the impurity existing in more than one site in the lattice (many cations
can exist either as interstitials or substitutionals).

Clearly, for the analysis leading to Eq. (5) to be useful in studying
this system, the first requirement is an accurate, simple and non-destruc-
tive means of measuring N_H. This requirement was recognized in our original
proposal and we pointed out there that the i r absorption band associated
with the H^+ provided a technique satisfying all of these requirements.
Utilization of this technique, however, required a very accurate determination
of the oscillator strength of this absorption band (i.e., the proportionality
constant relating N_H to the height of the absorption peak). This problem
proved to be a rather tough nut to crack. After considering several possible
approaches, we decided on the rather improbable technique of weighing the H
which had diffused into the crystal. This required determination of the
mass of a sample before and after H doping to an accuracy of almost 1 part
in 10^7. This proved to be even more difficult than we had anticipated, but
eventually we were successful in determining the oscillator strength to an
accuracy of ±3%.[12] The experiment was actually somewhat more complicated
than it sounds; because of the uncertainties in the properties of lattice

defects, it was necessary to use an isotope substitution technique, where H was replaced by D at equal concentrations. In retrospect, the return on our investment of time and effort on this measurement was enormous. The experimental tools provided by this measurement have proved to be the key to a wide variety of other measurements and have permitted us to make a great deal of progress in unravelling the very complex properties of this system. Measurement of N_H as a function of equilibration temperature and gas pressures and application of Eq. (5) yields not only the proton binding energy, E_B, but also the conduction band density of states, which can usually be determined only from electronic measurements. Having accurate values of these parameters, Eq. (5) can be used to determine the location of E_F in any crystal which has been equilibrated in a known ambient, independent of purity. This capability is of obvious importance for a wide variety of experiments and applications. Furthermore, knowledge of these thermodynamic parameters permits not only monitoring E_F, but provides the capability of positioning E_F at any desired level, by varying P_{O_2} and/or P_{H_2O}. This capability has already permitted us, for example, to obtain an equally quantitative technique for monitoring conduction electron density, n_c.[12] To do this, we simply compared the previously identified conduction electron absorption with the H^+ absorption band at different H concentrations. The ability to monitor n_c independently of electronic measurement is of extreme importance, as was discussed in Section I. This technique was used in conjunction with ESR measurements, for example, to establish the existence of four different charge states for substitutional Mo in TiO_2;[10] the number of potentially important studies of this sort which are now possible is virtually unlimited.

One further important bonus resulting from the H^+ oscillator strength measurement is that we can now apply these techniques as a means of determining sample purity with simple, non-destructive measurements. For example, if a specimen is equilibrated under conditions leading to measurable conduction electron concentration at room temperature, the difference between N_H and n_c is just the concentration of electron acceptor states in the crystals. Since virtually all cation substitutional impurities act as acceptors under these conditions, this is a good gauge of total impurity concentration. This technique has already proved to be invaluable in characterizing sample materials. A good deal of more detailed information is potentially obtainable in this way, since a series of measurements for various equilibration pressures and temperature would yield a plot of N_H vs. E_F, which is essentially amounts to a plot of electron trap density as a function of energy and hence, in principle, should make it possible to determine the concentration of individual impurities when their characteristic trapping levels have been obtained. The importance of this capability in relation ot our crystal growth program is again obvious.

Thus, in a very real sense, the H^+ absorption measurements have provided us with a "Rosetta Stone" which has made possible meaningful translation of the very complex language in which rutile has chosen to communicate with us. Clearly the work in this area will go on for some time; we have as yet only studied the tip of the iceberg.

B. Defect Thermodynamics.

The basic considerations in properly formulating the thermodynamics

for defects in a system such as TiO_2 are very similar to those encountered with H in the preceeding section. This problem has been discussed in detail in previous reports and it is sufficient to note that we have reformulated the existing theory to take proper account of variation of E_F.[6] The predictions of the theory are somewhat more complex than for H, due to the possibility of multiple charge states for the defects. The dependence on ambient pressures and temperature predicted are dramatically different, both for the two likely defects, the O vacancy and the Ti interstitial,[14] and for the different charge states of each.

As was previously mentioned, several thermodynamic studies of defects in TiO_2 had previously been done by other groups, with richly variable results. In view of the discussion in Section A above, the failure of these studies to produce definitive results is hardly surprising, particularly since the dependence of defect concentration on E_F is even more dramatic than in the case of H^+ because of the probable multiple charge of the defect. To make matters even worse, the high mobility of H^+ and its extreme importance in determining the thermodynamic behavior of TiO_2 was not recognized when these experiments were done. Thus, it is not possible to draw any conclusions from these studies, even though the proper theoretical tools are now available.

Accurate measurements of equilibrium defect concentration as a function of ambient pressures and temperature, together with knowledge of trap density and distribution (which can be obtained as outlined in Section A) provide ample information to determine the identity of the defect (or defects, if it should turn out that both O vacancies and Ti interstitials

-14-

are possible), and its charge state or states as well as the energy of formation. Unfortunately, these data are much more difficult to obtain than the H concentration data, since we have no means of directly measuring the defect concentration. Indirect measurements are possible by at least two different techniques, however. The first approach is to make all measurement in the range where E_F is high enough to yield significant concentrations of conduction electrons at room temperature. If the total electron trap density is known, the total number of electrons donated by the lattice defects is readily obtained since the conduction electron density can be measured optically. Unfortunately, this yields no direct information as to the number of defects involved, since the charge state is not known. However, the predictions of the theory are sufficiently distinctive for the various possibilities[6] that the identity and charge state can be inferred with confidence if enough data are available. We have carried these experiments far enough to obtain an approximate value for the energy of formation and to be reasonably confident that the dominant defect in the range near 800°C is the O vacancy and to determine that it has an electron trapping level ~0.3 eV below the conduction band. The data are less extensive than desirable at present due to the narrow range of experimentally accessible pressures, etc., and hence, these conclusions must be considered tentative. The second approach to this problem, while somewhat more complicated experimentally, appears to be more satisfactory, although it is clear that the measurements described above could, with patience, be refined enough to yield fairly accurate results. The alternative technique involves use of a stabilized ZrO_2 electrolytic cell to control and measure O_2 pressure. This is a technique which has been developed over the past

-15-

10 years and is now coming into fairly common use. The details of
the technique are described in Ref. 15, among others; for present purposes,
the system can be characterized as an electrolytic cell in which charge is
transported only by oxygen ions (O vacancies, actually). A known O_2 pressure
is maintained on one side of the electrolyte. If the O_2 pressure on the
other side is different, O will be transported through the electrolyte,
unless an appropriate retarding voltage is applied. Alternatively, if one
side of the cell is a sealed chamber, application of a voltage to the cell
results in oxygen transport into or out of the sealed chamber until the O_2
partial pressure appropriate to the applied voltage is established; this
pressure depends, of course, only on the thermodynamic properties of O_2,
which are well known. Thus, such a cell can be used to establish and
maintain a desired O_2 pressure. Furthermore, integration of the current
flow (i.e., measurements of the total charge transfer) when the applied
voltage (and hence, P_{O_2}) is changed, permits one to infer the change in O
vacancy or Ti interstitial concentration in a sample of TiO_2 contained in
the chamber, after taking account of the chamber volume, etc. Thus, we
have a very convenient means of monitoring the O uptake or release from our
specimen and from this information the change in defect concentration can
be obtained. Certain corrections for leakage currents, etc., are necessary,
but these are straightforward and readily checked. A further bonus of
this technique which should be mentioned is that these measurements can
be used to otain an accurate diffusion coefficient for the defect, since
the equilibration time depends only on diffusion of the defects (assuming
the cell temperature is high enough, etc.). Thus, supplementing the
techniques we are presently using with this type of measurement should
permit this problem to be solved once and for all.

C. Effects of Internal Fields on Diffusion and Distribution of Ions.

As discussed above, the influence of a "mobile" Fermi level on transport properties in wide gap semiconductors can be of overwhelming importance. An example of one such effect was considered in detail in an earlier paper on dielectric loss measurements on rutile[16]. It was shown that the presence of electrodes with work functions less than that of the rutile resulted in strong electric fields in the crystal which depleted a region near the surface of mobile positive ions and defects and considerably enhanced the electronic conductivity (~6 orders of magnitude) through the bulk of the crystal, while simultaneously producing thin, very high resistivity layers near the surface. The result was a high D.C. resistance, an apparent dielectric constant ~10^4 and a low resistivity over most of the sample.

The influence of these internal fields on macroscopic diffusion is of very far reaching importance and has been the major area of concentration during the last 1 1/2 years of this project. The detailed theory and experimental verification are presented in the attached papers[11]; hence, we will present only a brief qualitative description of the work here. There are two cases to consider: (1) The Fermi level is high enough that there are sufficient mobile electrons to maintain electron equilibrium at all times, so that the Fermi level is constant throughout the crystal. (2) The Fermi level is so low that there are essentially no mobile electrons, and hence the Fermi need not be the same everywhere. The first case leads to enhanced diffusion and the second to retarded diffusion.

The first case would apply, for example, to a TiO_2 crystal in which the Fermi level is not more than ~1 eV below the conduction band at the diffusion temperature. For the case of H diffusion (as described in the attached preprints), typical experimental conditions for bulk diffusion measurements

might be a temperature of ~700°C, in an atmosphere of O_2 and H_2O. In the attached preprints, we show that significant departures from charge neutrality cannot occur under these conditions and hence, the concentration of hydrogen (which enters the lattice as H^+) and electrons must be essentially equal. Thus, if the H^+ concentration changes significantly from one part of the specimen to another, the spacing between the Fermi level and the conduction band must also change. However, the Fermi level is the same everywhere, and hence the lattice bands must be warped up or down with a corresponding change in the electrostatic potential. Thus, any change in H^+ concentration necessarily leads to internal electric fields, the size of which depends on the density of states near the Fermi level. The smaller the density the greater the change in the lattice band - Fermi level spacing, and hence the greater the field for a given change in H^+ concentration. Thus, when the concentration of H is such as to just fill a major trap, the field, and hence the effective diffusion coefficient, will be a maximum. For most conditions the effective diffusion coefficient is a very sharply peaked function of H^+ concentration, resulting in a concentration profile (concentration vs position in the crystal at a given time) which is quite different from that expected from Fick's law. However, the total H content vs time curve is nearly indistinguishable from that predicted by Fick's law except that the apparent diffusion coefficient can be ~100 times that which would be observed in the absence of internal fields (i.e., the Fick's law coefficient) and is sample- and concentration-dependent. The exact value depends on the H concentration range covered in the experiment. Since many diffusion experiments have consisted simply of measuring total content of the diffusing specie as a function of time, the results thus obtained can be very misleading and disagreement between different experiments is to be expected. Obviously, these

considerations are in no way restricted to H or even to rutile. The effects are not dependent on crystal structure or the nature of the particular ion diffusing, but rather on the behavior of the Fermi level as a function of electron (and hence, impurity) concentration.

In the limiting case of no mobile electrons a coulomb field is set up by the charge separation (ions moving, electrons stationary) - as reflected in the variation in Fermi level from point to point in the crystal - which will block further diffusion and prevent any change in positive ion or defect concentration over macroscopic distances in the crystal. For example, Li in rutile has a very high diffusion coefficient ($\sim 10^{-6}$ cm^2/sec at room temperature). However, by lowering the Fermi level, for example, by Al doping, Li can be prevented from entering the crystal to any significant depth at temperatures where it would normally diffuse quite readily.

It is obvious that these effects have very far-reaching implications for diffusion properties in wide gap materials. In the first case, the apparent diffusion rate may be enhanced by 100x or more. In the second case, diffusion will be inhibited - sometimes by many orders of magnitude. The potential importance, for example, in solid electrolyte batteries is obvious as are the implications for a large number of other phenomena involving ionic diffusion.

We have succeeded in analyzing the first case in detail and have obtained excellent quantitative agreement between theory and experiment for the case of H$^+$ in TiO$_2$[11]. We have also devised an isotope exchange technique whereby the effects of internal fields can be virtually eliminated. Using this technique, we have measured the "true" (Fick's law) diffusion coefficients of H and D in rutile from 325 to 700°C[11]. The validity of our analysis is well established by the excellent agreement between experiment and theory, for

-19-

both single diffusion and isotope exchange measurements. Even more compelling evidence for both the validity and accuracy of these results, however, was obtained from independent measurements of H^+ mobility at much lower temperatures (100°C-200°C). Extrapolation of the bulk diffusion data to this lower range agreed extremely well with measurements of AC conductivity on an Al-H doped specimen in which the Fermi level had been adjusted to essentially eliminate electronic conductivity[11].

D. ESR Measurements and Miscellaneous Projects.

An important experimental tool for work on rutile is ESR. When combined with the optical and thermodynamic studies already discussed, it has proved a very powerful and valuable technique. An early achievement with ESR was to establish unambiguously that "vacuum" reduction does not take place at a significant rate below 1000°C[9]. As previously mentioned, the frequently observed reduction is due to contaminants in the vacuum system. These ESR results dramatically illustrated the importance of proper sample characterization. When combined with optical measurements, ESR work also provided a very striking demonstration of the effect of variation of the Fermi level. It was shown that Mo in rutile can exist in 4 different charge states[10]: 6+, 5+, 4+, and 3+. Due to the large dielectric constant of TiO_2, it is likely that most impurities will have multiple charge states. In addition to demonstrating the overriding importance of Fermi level in wide gap materials, this work also demonstrated the necessity for use of more than one technique, since only two of the Mo states, 5+ and 3+, could be seen directly with ESR. The use of a technique-oriented rather than material-oriented approach has led others to the erroneous conclusion that Mo existed only in the 5+ state normally seen with ESR and obscured the central fact of the importance of Fermi level. Again, coupling ESR measurements with the optical and

thermodynamic work discussed above led to correction of an important and widely accepted identification of a particular ESR spectrum. The major significance is that this spectrum has been identified with Ti^{3+} interstitials and constituted the major evidence for Ti interstitials being the dominant lattice defect. Our work showed that the spectrum actually was associated with H rather than with Ti interstitials.[14]

Substitutional Fe is one of the major important impurities in TiO_2, particularly since the solubility is very high. It is also important because of the maser applications of Fe-doped TiO_2. ESR studies, again coupled with controlled H doping and optical measurements, permitted us to identify the charge states of the Fe and the associated optical absorption spectra, and also led to the identification of a perturbed ESR spectrum which results from trapping of an H^+ near the Fe substitional. These results confirmed our previous speculations as to the equilibrium site of the H^+, and open the way for interesting studies of the low temperature kinetics of H^+ in rutile.

Perhaps the main lesson of the ESR work is the clear importance of combining several techniques to attack problems in materials of this complexity. In addition to the obvious fact that interpretation is much surer, an equally important effect is that the material-oriented approach leads to the right questions being asked. Thus, instead of compiling an interesting, but unrelated set of facts, one is able to answer questions of really central importance for development of the field.

A relatively small, but nonetheless important area of effort during this project has been the construction of a Fourier Transform IR spectrometer. This instrument should prove to be of great value in subsequent work on rutile and similar systems. The construction has been financed primarily

by the department, but we have been closely associated with the project because of its potential usefulness on rutile.

Finally, an area of considerable effort has been the writing of a review paper on rutile. The field has developed so rapidly during the past four years that it has not yet seemed appropriate to close the paper. In particular, a wide range of previously held interpretations have been overturned by the work described above on the effects of variation of Fermi level on solubility and diffusion of defects and impurities. We anticipate establishing a cutoff date of September 1, 1974, and hence, submission of the paper by the end of 1974.

E. Appropriate Future Research in TiO_2.

In this Section we will outline the problems which can now be attacked with reasonable hope of success. As discussed in Section I this means that sufficient background information has been acquired that the correct way to do and interpret the experiments is now clear. The most promising areas appear to be listed below.

1. Determination of the identity and thermodynamic parameters of the dominant defect.

2. Measurement of conduction band parameters, including effective density of states and drift mobility.

3. The trapping levels and thermodynamic parameters of major impurities.

4. Determination of the importance of impurity band and valence band conduction, and the parameters necessary to characterize the bands in which important conduction exists.

5. Analysis of the parameters necessary to properly match electrodes and electrolyte in an impurity based solid electrolyte of the rutile "family".

6. Study of the feasibility of use of the Li-rutile system as an electrolyte.

-22-

These problems seem particularly appropriate at this time and we will be proposing work on them to various agencies in the near future.

In addition to these problems, there are a set of "second generation" questions which probably cannot be attacked successfully at present but which are important and will become appropriate topics when the above work is completed. These include:

1. Determination of the sources of the well-known D.C. instability.

2. Exploration of the feasibility of making electronic devices based on the rutile system.

3. Theoretical analysis of polaron conduction in rutile.

4. Application of single crystal results to polycrystalline and, if possible, amorphous TiO_2.

III. RESULTS OF THE CRYSTAL GROWTH PROGRAM

It was clear at the outset of this program that if we were ever to attain the long range goals discussed above, we would eventually require far better sample material than was available at that time. On the other hand, there was also a great deal of work which needed to be done (particularly development of sample characterization techniques and thermodynamic studies) before better crystals would be any particular advantage -- or for that matter, before we could confidently distinguish between "good" and "bad" crystals. The value of careful long-range planning is clearly demonstrated by the developments during the past four years. We have now reached the stage where the quality of commercially available crystals would soon limit further progress; our crystal growth group has now reached the point where it is clear that they can produce substantially superior crystals. Furthermore, we have made excellent progress in developing sample evaluation techniques (see Section II-B), and the crystal growth program is now at the stage where such techniques will be required to improve further the quality of crystals produced. Thus the two parts of the program have dovetailed very nicely, to the mutual benefit of both.

A preliminary survey of possible techniques for the growth of TiO_2 convinced us that none of the methods in use at the beginning of the program could be developed sufficiently to produce the quality required, and it was necessary to develop an entirely different approach. The technique selected as the most promising was that of chemical vapor transport, in which the TiO_2 is transported from source material at one end of a sealed quartz ampoule to a seed cyrstal at the opposite end, by means of the reversible reaction

$$TiO_2(s) + TeCl_4(g) \leftrightarrow TeO_2(g) + TiCl_4(g)$$
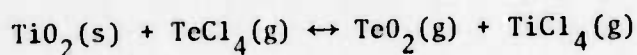
The advntages of this technique are too numerous to discuss in detail, but

-24-

of particular importance is the fact that substantial growth occurs even 1000°C below the melting temperature, in a sealed system, thus making it possible, at least in principle, to attain extremely high purity.[17] Furthermore, growth occurs under essentially isothermal conditions, thus eliminating the second major problem with commercially available crystals, that of residual thermal strains and high dislocation and grain boundary content. Thus the prospects for ultimately obtaining first rate sample material were very promising. Since this growth technique had not previously been applied to TiO_2 (and only in a very limited way to other systems), we anticipated that unforeseen problems would arise in the development of the technique and we were certainly not disappointed in this respect. However, none of the problems proved to be insurmountable and the overall progress has been very gratifying. In Section A below, we will discuss some of the more significant problems and the progress we have made in solving them. A substantial part of the work which was required to achieve success in growing TiO_2 was of a very fundamental nature and its importance is not limited to the growth of TiO_2 or even to chemical vapor transport problems in general; we will briefly summarize the most important results in Section B, and give a short "status report", summarizing the present "state of the art", and in Section C we will outline the remaining problems and the work planned for the immediate future.

A. <u>Problems Encountered in Developing Chemical Vapor Transport Technique.</u>

The first difficulty which had to be overcome was that of a suitable furnace. Briefly, the major requirements were: (1) Low thermal inertia to permit rapid temperature changes (2) Two temperature zones, with very sharp transition (~1 inch) between zones (3) Very precise temperature control for each zone independently (4) Optical viewing ports for observing the crystal during growth. There were no commercially available furnaces satisfying

-25-

these requirements; considerable development work and several novel inno-
vations eventually culminated in a very satisfactory design, which was
described in an earlier report.[17] These furnaces are inexpensive, durable
and have the added advantage that they are readily scaled up in size from
the present model to permit growth of large crystals.

Although the basic idea of this technique of crystal growth is quite
simple, the details of the transport process are extremely complex, and com-
plete understanding requires not only accurate and detailed knowledge of the
thermodynamics of all of the gas and solid phases present, but also must
take account of the kinetics of the reactions and the hydrodynamic behavior
of the gases. Several difficulties were encountered in this general area.
Ideally, transport should occur primarily by gaseous diffusion, perhaps
aided somewhat by slow convection currents. Rapid convection, and particularly
turbulent flow of the gases, must be avoided, since this would lead to tem-
perature instability at the growing seed, with disastrous consequences.
Preliminary calculations indicated that only mild convection currents would
be encountered with the small temperature differential necessary to produce
satisfactory growth rates. However, it was immediately obvious that this
condition was not being achieved; wildly turbulent flow was readily observable
through the viewing port. A special ampoule was constructed with several
built-in thermocouples, and we found temperature oscillations of as much as
$\pm$ 25°C throughout the ampoule under growth conditions. When the $TeCl_4$ was
replaced by an inert gas at the same pressure, the oscillations disappeared
completely, thus suggesting that the convective instability was being driven
by a chemical reaction in the gas phase. Further investigation showed that
indeed this was the case, the main contribution being the pressure change
accompanying the dissociation of $TeCl_4$ into $TeCl_2$ and Cl_2.[18]

This observation led us to the conclusion that the published thermodynamic data on $TeCl_4$ were in error. Subsequent measurements of pressure vs. temperature of $TeCl_4$ in a closed quartz Bourdon gauge permitted us to make the first accurate measurement of the energy of dissociation of $TeCl_4$.[19] On the basis of the insight obtained through these studies and the revised thermodynamic data, we were able to eliminate the problem of temperature instabilities by appropriate modifications of the growth conditions.

Contaminants in commercially available $TeCl_4$ proved to be a serious difficulty during the early runs. This problem was eliminated by using high purity metallic Te and gaseous Cl_2, and allowing them to react inside the growth ampoule. Again, the best commercially available Cl_2 proved to be unsatisfactory, due to contamination (mainly HCl) and it was necessary to develop a Cl_2 distillation system.

Some difficulties were encountered with parasitic growth of TiO_2 crystals on the wall of the ampoule. We made some progress in eliminating this problem simply by exercising extreme care in clearning the ampoule to eliminate nucleation sites, and by carefully controlling the temperature differential between the ends of the ampoule. The final solution, however, involved a rather elegant innovation. Because the emissivity of TiO_2 is much higher than that of fused quartz, it is actually possible to keep the growing TiO_2 crystal at a slightly lower temperature than the surrounding ampoule, by providing weak optical coupling to the outside of the furnace, thus permitting slight radiative cooling of the seed.[20] This technique proved to be very effective and essentially eliminated spontaneous nucleation on the ampoule walls.

It is essential that the growing crystal not be allowed to touch the walls of the ampoule, since it adheres very strongly and the difference in thermal contaction on cooling invariably results in fracturing the TiO_2 crystal. Thus, a technique for suspending the seed crystal away from the ampoule walls was essential. This has been accomplished by drilling a hole in the seed and suspending it from a small quartz hook. The quartz hook causes some initial perturbation of the crystal perfection as it grows around the hook, but the perturbed growth is confined to a small part of the crystal and causes no serious difficulty. However, contact with the quartz hook still frequently results in fracture of the crystal on cooling. In most cases, most of the crystal is still usable, but complete elimination of the problem would be very desirable. It appears that it will be possible to eliminate this problem by replacing the solid quartz hook with a hollow one, fabricated from a very thin capillary. If this technique is not satisfactory, we can eliminate the difficulty by using a long, thin seed loosely attached to the end of the ampoule. We do not anticipate serious difficulties in eliminating this problem completely.

The limited thermodynamic data available on the Si-Cl-O system indicate that some Si transport from the ampoule walls is possible under growth conditions. However, mass spectrographic analysis[21] indicates that the concentration of dissolved silicon in crystals we have grown is quite small (≤ 20 PPM). Such a concentration would probably be quite tolerable; Si would be unlikely to effect any of the properties of the crystal in a significant way, since it has the same valence as Ti. Optimization of growth parameters will undoubtedly permit us to lower this concentration substantially in any event, so it does not appear that dissolved Si constitutes a significant

-28-

problem. However, a more troublesome aspect of the Si transport problem has been the sporadic occurrence of SiO_2 inclusions in the TiO_2 matrix. Aside from early runs in which the growth temperature and source-seed temperature differential were too high, these inclusions have been observed only as a result of nucleation at the surface of the original seed. The SiO_2 inclusions do not always occur -- one batch of seed crystals, cut from a single parent crystal, have consistently produced crystals without inclusions. While this problem is not yet fully understood, it appears that the mechanism responsible for the SiO_2 inclusions involves Si impurity in the seed crystal. The seed crystals are etched in situ, by reversing the normal temperature profile before growth is started, in order to eliminate damage due to handling, etc. It appears that the sequence of events leading to formation of SiO_2 inclusions is as follows; a seed crystal, containing significant concentrations of Si (or possibly some other unknown impurity) is etched under conditions in which Si is not transported away from the seed at a significant rate and hence, the Si impurities originally in the seed remain on the surface and form nucleation sites for later growth of SiO_2. If this interpretation, which is presently being tested, is correct we will have no difficulty eliminating the inclusions. In any event, the fact that some seed material invariably produces inclusion-free growth essentially guarantees that the problem can be solved, though some patience may be required to isolate the exact cause of the problem.

A considerable amount of work remains to be done, of course, particularly with respect to optimization of growth parameters. There are strong indications that substantially higher growth rates can be achieved without

sacrificing quality, and that significantly lower growth temperatures are possible. As yet, no work has been done on purification of starting material, nor have we attempted to study the transport of impurities in the source material. Nevertheless, the feasibility of growth of the "next generation" of TiO_2 crystals by this technique is clearly established, and there is every reason to believe that all of our original high expectations will be realized.

B. Summary of Major Achievements of the Crystal Growth Program.

1. The dramatic improvement in quality of crystals grown by chemical vapor transport and the viability of this technique for production of research-grade crystals has been clearly demonstrated.

We are now routinely producing cm size crystals of purity significantly better than commercially available crystals, despite the fact that they are grown from reagent grade starting material and no attempt has been made to improve the purity as yet. The mechanical perfection appears to be vastly superior to commercial materials. We have achieved growth rates of ≥ 2 mm/week and anticipate that substantially higher rates can be attained without sacrifice of quality.

In addition to the accomplishment of our major goal of developing a new technique for production of the high quality TiO_2 crystals, several significant advances of a fundamental and more generally applicable nature were made in the course of this research:

2. Discovery and analysis of chemically driven convective instability and attendant temperature oscillations.[18]

3. Development of a generally useful technique for measurement of dissociation of gases at elevated temperatures, leading to accurate thermodynamic data on dissociation of $TeCl_4$.[19]

4. Development of a novel furnace design of general usefulness in this type of crystal growth.

5. Development of a technique for eliminating parasitic crystal growth on ampoule walls.[20]

C. Plans for Future Research on Growth of TiO_2 Crystals by Chemical Vapor Transport.

To take full advantage of this new technique for production of TiO_2 crystals, a considerable amount of work is still required. As discussed in Section IIB, techniques for sample characterization have been developed and we are now ready to attack the problem of sample purity. The first step clearly is that of improving the quality of starting material. The properties of the Ti halides are such that high purity should be readily attainable. Studies of impurity transport under growth conditions should be undertaken in order to optimize crystal purity, but also to permit controlled doping with impurities such as Mo and W which cannot be introduced by diffusion. Detailed studies of sample perfection (dislocation and grain boundary content) are also needed as part of a program to optimize growth parameters. Again, suitable sample characterization techniques have already been developed.[22]

In addition to these rather fundamental questions, an analysis of the

-31-

overall growth process aimed at improving the economics of crystal production will soon be needed and the present crystal growth equipment will need to be scaled up for the production of larger crystals.

Finally, a careful study of the possibility of applying this growth technique to similar systems should be undertaken.

IV. REFERENCES

1. ARPA Technical Report for period ending November 30, 1971, #DAHC 15-71-G8 and ARPA Technical Report for period ending July 31, 1972, #DAHC 15-71-G8.

2. V. N. Bogomolov, Yu. A. Firsov, E. K. Kudinov, and D. N. Mirlin, Phys. Stat. Sol. 35, 555 (1969).

   M. I. Klinger, Phys. Stat. Sol. 27, 479 (1968).

3. 1. Bransky and D. S. Tannhauser, Solid State Comm. 7, 245 (1969).

   R. R. Hasiguti, E. Yagi and M. Aono, Radiation Effects 4, 137 (1970).

4. J. Appel. Polarons, Solid State Physics, Vol. 21, 1968, Editors: F. Seitz, D. Turnbull, H. Ehrenreich, Academic Press, New York.

5. G. A. Acket, Thesis, University of Utrecht (1965).

6. J. W. DeFord and O. W. Johnson, J. Appl. Phys. 44, 3001 (1973).

7. Von Hippel, J. Kalnajs and W. B. Westphal, J. Chem. Phys. Solids 23, 779 (1962).

8. L. N. Shen, O. W. Johnson, W. D. Ohlsen and J. W. DeFord, scheduled to appear in Phys. Rev. B, Sept. 1, 1974.

   E. Iguchi and K. Yujima, Trans. Jap. Inst. Metals 13, 45 (1972) and J. Phys. Soc. Jap. 32, 1415 (1972).

   L. E. Hollander and P. L. Castro, Phys. Rev. 119, 1882 (1960).

   P. L. Kingsbury, Jr., W. D. Ohlsen and O. W. Johnson, Phys. Rev. 175, 1091 (1968).

   P. F. Chester, J. Appl. Phys. 32, 2233 (1961).

9. W. D. Ohlsen and O. W. Johnson, J. Appl. Phys. 44, 1927 (1973).

10. W. D. Ohlsen, Phys. Rev. B 7, 4058 (1973).

11. J. W. DeFord and O. W. Johnson, "Anomalous Diffusion in Non-Metals (Origin and Effects of Internal Electric Fields)", submitted to J. Appl. Phys. (1974).

References (con't)

O. W. Johnson, J. W. DeFord and S.-H Paek, "Diffusion of H and D in TiO$_2$: Suppression of Internal Fields by Isotope Exchange", submitted to J. Appl. Phys. (1974).

O. W. Johnson, J. W. DeFord, "Simultaneous Diffusion of Two or More Ions in the Presence of Internal Electric Fields", submitted to J. Appl. Phys. (1974).

12. O. W. Johnson, J. W. DeFord and J. W. Shaner, J. Appl. Phys. 44, 3008 (1973).

13. R. G. Breckenridge and W. R. Hosler, Phys. Rev. 91, 793 (1953).

    K. S. Förland, Acta Chem. Scand. 20, 2573 (1966).

    D. C. Cronemeyer, Phys. Rev. 113, 1222 (1959).

    C. J. Kevane, Phys. Rev. 133, A1431 (1964).

    P. Kofstad, J. Phys. Chem. Sol. 23, 1579 (1962).

14. L. N. Shen, O. W. Johnson, W. D. Ohlsen and J. W. DeFord, scheduled to appear in Phys. Rev. B, Sept. 1, 1974.

15. K. Kiukkola and C. Wagner, J. Electrochem. Soc. 104, 308 (1957).

    K. Kiukkola and C. Wagner, J. Electrochem. Soc. 104, 379 (1957).

    I. Heyne, "Ionic Conductivity in Oxides", Proceedings, National Bureau of Standards Symposium on Mass Transport in Oxides, October 1967, NBS Special Publication 296, p. 149-164 (1968).

    T. H. Etsell and S. N. Flengas, Chemical Review 70, 339 (1970).

16. O. W. Johnson, J. W. DeFord and S. Myhra, J. Appl. Phys. 43, 807 (1972).

17. ARPA Technical Report for period ending June 30, 1971, #DAHC 15-70-G13.

18. F. Rosenberger, M. C. DeLong and J. M. Olson, J. Crystal Growth, 19, 317 (1973).

References (con't)

19. F. Rosenberger and M. C. DeLong, "The Standard Gibbs Energy of
    Dissociation of $TeCl_4$ Between 670 and 1170°K", J. Chem. Thermodynamics
    (in press).

20. ARPA Technical Report for period ending July 31, 1972, #DAHC 15-71-G8.

21. ARPA Technical Report for period ending August 15, 1973, #DAHC 15-73-G2.

22. O. W. Johnson, J. Appl. Phys. 35, 3049 (1964).

V. TALKS AND PAPERS RESULTING FROM THIS PROJECT

The following papers have been published:

1. "Dielectric Loss Mechanism in Rutile (TiO_2)", O. W. Johnson, J. W. DeFord and S. Myhra, J. Appl. Phys. 43, 807 (1972).

2. "'Vacuum Reduction' of Rutile", W. D. Ohlsen and O. W. Johnson, J. Appl. Phys. 44, 1927 (1973).

3. "Experimental Technique for the Precise Determination of H and D Concentration in Rutile (TiO_2)", O. W. Johnson, J. W. DeFord and J. W. Shaner, J. Appl. Phys. 44, 3008 (1973).

4. "Defect and Impurity Thermodynamics in Rutilelike Systems", J. W. DeFord and O. W. Johnson, J. Appl. Phys. 44, 3001 (1973).

5. "Variation of Crystal Fermi Energy as a Method of Obtaining Different Charge State of Ions for ESR Study", W. D. Ohlsen, Magnetic Resonance and Related Phenomena, edited by V. Hovi (North Holland Publishing Co., Amsterdam, 1973), p. 513.

6. "Electron-Spin-Resonance Studies of Mo^{6+}, Mo^{5+}, Mo^{4+}, and Mo^{3+} in Rutile", W. D. Ohlsen, Phys. Rev. B 7, 4058 (1973).

7. "General EPR Parameter Fitting Program", W. D. Ohlsen, #243 of the Quantum Chemistry Program Exchange, Indiana University, Chemistry Department, accepted 1973.

8. "Heat Transfer and Temperature Oscillations in Chemical Vapor Transport Crystal Growth I", F. Rosenberger, M. C. DeLong, and J. M. Olson, J. Crystal Growth, 19, 317 (1973).

9. "Gruneisen γ of Rutile (TiO_2)", J. W. Shaner, Phys. Rev. B, 7, 5008 (1973).

10. "The Standard Gibbs Energy of Dissociation of $TeCl_4$ Between 670 and 1170°K", F. Rosenberger and M. C. DeLong, J. Chem. Thermodynamics (in press).

The following papers have been accepted for publication:

1. "Re-Interpretation of the 'Ti^{3+} Interstitial' ESR Spectrum in Rutile", L. N. Shen, O. W. Johnson, W. D. Ohlsen, and J. W. DeFord, Phys. Rev. B, to be published, Sept. (1974).

2. "Concentration Dependent Diffusion of H$^+$ in TiO$_2$: Analysis of Electronic Effects in Ionic Diffusion", O. W. Johnson, J. W. DeFord, S.-H Paek, Proceedings of the Ninth University Conference on Ceramic Science, to be published late 1974.

3. "Hyperfine Structure of Fe^{3+} Ions in Rutile (TiO$_2$)", W. D. Ohlsen and L. N. Shen, J. Phys. Soc. Japan, to be published late 1974.

The following papers have been submitted for publication:

1. "Anomalous Diffusion in Non-Metals (Origin and Effects of Internal Electric Fields)", J. W. DeFord and O. W. Johnson, submitted to J. Appl. Phys. May, 1974.

2. "Simultaneous Diffusion of Two or More Ions in the Presence of Internal Electric Fields", J. W. DeFord and O. W. Johnson, submitted to J. Appl. Phys. May, 1974.

3. "Diffusion of H and D in TiO$_2$: Suppression of Internal Fields by Isotope Exchange", O. W. Johnson, S.-H Paek and J. W. DeFord, submitted to J. Appl. Phys. May, 1974.

4. "The Band Gap Absorption of Rutile (TiO$_2$)", J. Shaner, to be submitted to Phys. Rev. Letters, 1974.

The following oral papers have been presented:

1. "'Vacuum Reduction' in Rutile", W. D. Ohlsen and O. W. Johnson, presented at the American Physical Society Meeting in Washington, D. C., April, 1972. Abstract in Bull. Am. Phys. Soc. $\underline{17}$, 618 (1972).

2. "Optical and Electronic Properties of Mo in TiO_2", J. W. DeFord and O. W. Johnson, presented at the American Physical Society Meeting in Washington, D. C., June, 1972.

3. "Variation of Crystal Fermi Energy as a Method of Obtaining Different Charge States of Ions for ESR Study", W. D. Ohlsen, presented at the XVII Congress Ampere in Turku, Finland, August, 1972.

4. "Growth of TiO_2 (Rutile) by Chemical Vapor Transport", F. Rosenberger and M. C. DeLong, presented at the Second National Conference on Crystal Growth, July, 1972.

5. "Heat Transfer and Temperature Oscillations in Chemical Vapor Transport", F. Rosenberger, M. C. DeLong and J. M. Olson, presented at the Second National Conference on Crystal Growth, July, 1972.

6. "Heat and Mass Transfer Effects in Chemical Vapor Crystal Growth", F. Rosenberger, seminar given for the Department of Physics, Purdue University, Indiana, August, 1972.

7. "Growth of Rutile Single Crystals by Chemical Vapor Transport", F. Rosenberger and M. C. DeLong, presented at the American Ceramic Society meeting in Portland, Oregon, October, 1972.

8. "Heat Transfer and Temperature Oscillations in Chemical Vapor Crystal Growth", F. Rosenberger, M. C. DeLong and J. M. Olson, presented at the American Physical Society meeting, Los Angeles, California, December, 1972.

9. "ESR Evidence for a $Fe^{3+} \cdot H$ Center in Iron-Hydrogen Doped Rutile", W. D. Ohlsen and O. W. Johnson, presented at the American Physical Society meeting in San Diego, California, March, 1973. Abstract in Bull. Am. Phys. Soc. 18, 466 (1973).

10. "Defect and Impurity Thermodynamics in Rutilelike Systems", J. W. DeFord and O. W. Johnson, presented at the American Physical Society meeting in San Diego, March, 1973.

11. "Heat and Mass Transfer Phenomena in CVT Crystal Growth", F. Rosenberger, M. C. DeLong and J. M. Olson, presented at the Gordon Research Conference on Crystal Growth, Tilton, New Hampshire, July, 1973.

12. "An Experimental Technique for the Precise Determination of H and D Concentration in Rutile (TiO_2)", O. W. Johnson and J. W. DeFord, presented at the American Physical Society Meeting in San Diego, March, 1973.

13. "Morphological Stability Concepts in Crystal Growth", F. Rosenberger, invited paper given at Rockwell International, Anaheim, California, November, 1973.

14. "Stability Considerations in Fluid-Solid Phase Transitions", F. Rosenberger, seminar presented at the National Atomic Energy Commission of Mexico, November, 1973.

15. "An Identity Crisis for the Ti^{3+} Interstitial in Rutile", O. W. Johnson, W. D. Ohlsen and L. N. Shen, presented at the American Physical Society meeting in Philadelphia, March, 1974. Abstract in Bull. Am. Phys. Soc. 19, 328 (1974).

16. "Concentration Dependent Diffusion of H^+ in TiO_2: Analysis of Electronic Effects in Ionic Diffusion", O. W. Johnson, J. W. DeFord and S.-H. Paek, invited paper presented at the Ninth University Conference on Ceramic Science in Cleveland, Ohio, June, 1974.

17. "Hydrogen and Deuterium Diffusion in Rutile", J. W. DeFord and O. W. Johnson presented at the American Physical Society meeting in Philadelphia, March, 1974.

18. "Transport Phenomena and Morphological Stability in Vapor Crystal Growth", F. Rosenberger, invited paper given at the Gordon Research Conference on Crystal Growth, New Hampshire, July, 1974.